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Transparent nano-glass-ceramic for photonic applications. Distribution of RE-doping elements in the fluoride nano-crystals analysed by XAS and HR-TEM

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Abstract. Rare-earth (RE) ions-doped oxyfluoride transparent glass-ceramics containing nano-crystalline phases with very low phonon energies like LaF_3, $NaLaF_4$ and $KLaF_4$ combine the superior optical performance of low phonon energy phases with the high mechanical, chemical and thermal stability of oxide silicates. The insertion of the doping RE ions in the fluoride nanocrystals enhances the radiative optical emission processes currently focused on up- and down-conversion emissions. Thus, a key point is to identify and quantify the RE ions in the fluoride nano-crystals. In this contribution an oxyfluoride glass and the corresponding glass-ceramics of composition 55 SiO_2. 20 Al_2O_3.15 Na_2O.10 LaF_3 mol % doped with 1 mol % Tm_2O_3 is presented. The Tm^{3+} incorporation in the precipitated LaF_3 nano-crystals has been analysed by two different techniques. Firstly, TEM and Energy Dispersive X-Ray Spectroscopy (EDXS) were used to perform elemental distribution mappings of RE elements that allow to directly localising RE ions in the glass and glass-ceramics. Additionally, X-ray absorption spectroscopy (XAS) measurements were performed to analyse the distribution and first coordination sphere of Tm^{3+} ions in the glass and glass–ceramics by using X-ray absorption near edge structure spectroscopy (XANES) and extended absorption X-ray fine structure spectroscopy (EXAFS), which have allow to quantify the Tm^{3+} incorporation in the LaF_3 nano-crystals.

Introduction

The development of optical devices based on materials doped with rare earth (RE) ions is ongoing. In that sense, the preparation of oxyfluoride glass-ceramics offers a better alternative to the current phosphate glasses or fluoride crystals, since they combine the low phonon energy, optical transparency and RE ion solubility typical of fluoride matrices, with the good mechanical, thermal and chemical properties of oxide glasses. It is well known that the partial distribution of the doping RE ions in the fluoride crystalline phase of the glass-ceramic enhances the radiative optical emission processes currently focused on up- and down-conversion emissions [1] . For this reason, a key point to confirm the suitability of these glass-ceramics for optical applications is to identify and quantify the inclusion of rare earth ions in the precipitated fluoride phases.

Our investigations are focused on glasses and glass-ceramics in the system Na_2O-K_2O-Al_2O_3-SiO_2-LaF_3, as precursors of transparent glass-ceramics [2-34]. The composition of the glasses has been proved to extremely influence the precipitated crystalline phase in the glass-ceramics, being simple or mixed fluorides [2-345], and also in the crystallisation kinetics. The phase separation phenomena in the parent glasses have also a strong effect on further crystallisation processes [6].

The design of different compositions has allowed the devitrification of three different crystalline phases: LaF_3 [2,7], $NaLaF_4$ [3] and $KLaF_4$ [4]. It was demonstrated that the temperature and time of the heat treatments influence the size and the crystalline fraction in the glass-ceramics.

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For elucidating the crystallisation mechanism, compositional changes in the glassy matrix with heat treatment are particularly important; indeed, if the viscosity increases at the interface, it will act as a diffusion barrier that will notably decelerate the crystal growth velocity.

EELS and EFTEM techniques have been decisive in confirming the formation of a silica enriched barrier around the crystals (Fig.1) [3].

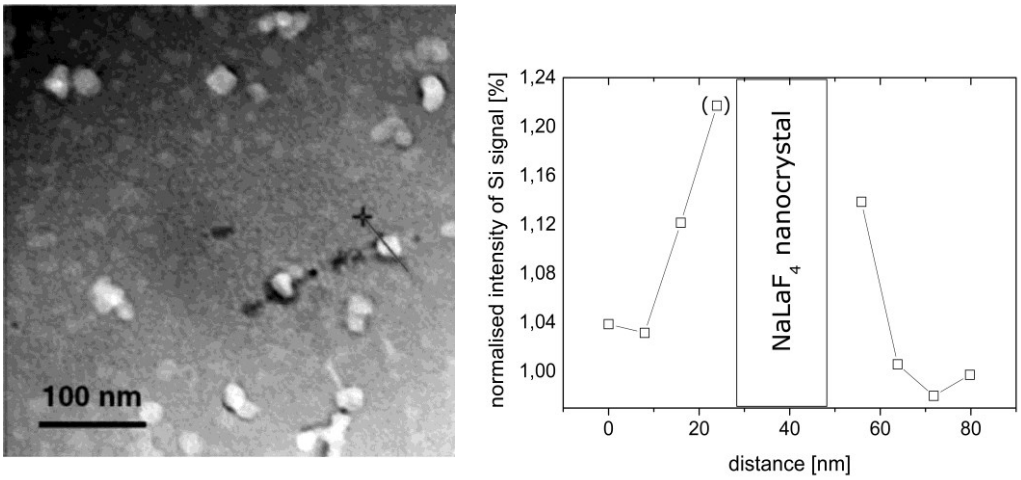

Figure 1: Left: Dark field STEM image of the $NaLaF_4$ glass-ceramic, with the location of spot analysis indicated. Right: Normalized Si intensity along the trace of the line across a $NaLaF_4$ nano-crystal [3].

Thus, the crystallisation mechanism of fluoride species was deduced to take place as follows [2]: phase separation regions rich in La, fluorine and silicon are formed. The thermal treatment of the glass results in the growth of the corresponding fluoride crystals (LaF_3, $NaLaF_4$, $KLaF_4$) inside the phase separation droplets, the crystal size being limited by the size of these droplets. Silicon redistributes around the crystals forming a shell which inhibits further crystal growth.

Once the nano-crystallisation mechanism was understood, the glass compositions were doped with lanthanide ions, in order to obtain luminescent properties, mainly focussed on up-conversion (UC) emission. Through UC processes it is possible to obtain visible light (blue, red, green, depending on the RE doping ions) from longer wavelength radiation (near infrared, infrared). The addition of RE ions has been proved to modify the glass structure and crystallisation processes, mainly reducing the fluorine loss and modifying the extension of phase separation in the glasses. In general, a delay in the beginning of crystallisation has been observed with the addition of lanthanide ions [8,9].

The optical characterisation of the studied glasses and glass-ceramics confirmed the partial incorporation of RE ions like Tm^{3+} and Eu^{3+} into the fluoride crystals [8]. In the Tm^{3+} - doped glass and glass-ceramic of composition $70SiO_2.7Al_2O_3.8Na_2O.8K_2O$. 7 LaF_3 mol %, where $NaLaF_4$ nano-crystals precipitated, blue UC emission at around 450 nm is obtained from excitation at 790 nm, through a mechanism in which 2 photons are involved (Fig.2)[8]. The measured UC emission is more intense in the glass-ceramics than in the parent glasses, likely due to the location of the RE ions in the crystalline phase [9]. Most papers in literature discuss the distribution of RE ions in the glass-ceramics taking into account only optical results.

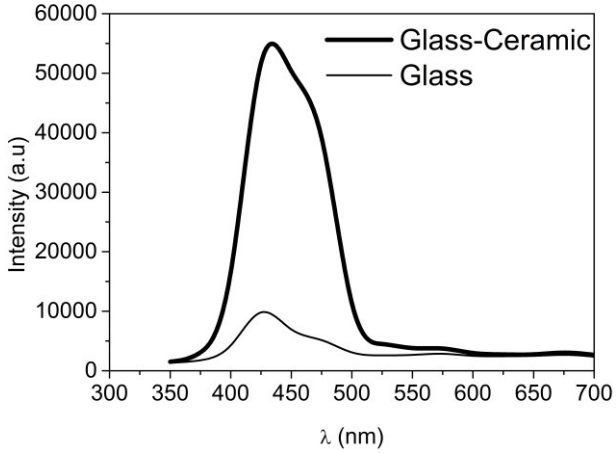

Figure 2: Up-conversion emission spectra of the $NaLaF_4$ glass and glass-ceramic doped with Tm^{3+}, from 790 nm excitation [9,10].

In the present contribution, the use of TEM and EDX and XAS are presented as excellent tools for the evaluation of the distribution of RE ions in oxyfluoride nano-glass-ceramics, including the quantification of these ions into the fluoride nano-crystals [11,12].

Transmission Electron microscopy (TEM) has proved to be a very useful technique in the characterisation of glasses and glass-ceramics. In the past decade, aberration correction and new detectors became available, constituting the new generation of transmission electron microscopes. Aberration correction facilitates imaging and analytics at much reduced acceleration voltages (80 or even 60 keV instead of 300 keV) while still keeping a spatial resolution unsurpassed by other techniques. Low acceleration voltages are particularly favourable to reduce radiation damage of electron beam sensitive oxyfluoride glasses. To the best of our knowledge, to date, no studies exist concerning the particular distribution of RE ions in oxyfluoride glass-ceramics, based on TEM techniques, like Energy Dispersive X-Ray Spectroscopy (EDXS). The possibility to perform elemental distribution mappings of RE elements has allowed to directly localising Tm^{3+} ions in the studied oxyfluoride glass and glass-ceramics.

On the other hand, X-ray absorption spectroscopy (XAS) possesses a great selectivity to discern different local chemical environment of an element. Thus, XAS is especially attractive for studying disordered materials. In this paper, we analyse the distribution and first coordination sphere of Tm^{3+} ions in the studied oxyfluoride glass and glass-ceramics by using X-ray absorption near edge structure spectroscopy (XANES) and extended absorption X-ray fine structure spectroscopy (EXAFS), which have allowed to quantify the relative concentrations of Tm^{3+} in the glass matrix and fluoride nano-crystals, a key issue to apply these materials in optics and optoelectronic.

Materials and Methods

A glass of nominal composition (in mol. %) $55SiO_2{\cdot}20Al_2O_3{\cdot}15Na_2O{\cdot}10LaF_3$ doped with 1 mol.% of Tm_2O_3 was prepared according with the procedure in Ref. [8]. Glass-ceramics were obtained by heating the parent glass in an electric furnace, at 620 °C during 10 and 40 h. The complete chemical, thermal and structural characterisation of the glass and glass-ceramics was reported in Ref.[8] .

TEM sample preparation was developed by grinding and polishing. The TEM analysis of the samples was done on an FEI Titan 3 80-300 electron microscope (FEI Company). Due to the extreme sensitivity of the samples, the acceleration voltage was reduced to 80 kV. Besides TEM analysis, STEM with a high angle annular dark-field (HAADF) detector was performed on the

samples as well, using the same electron microscope. In combination with energy dispersive X-ray spectroscopy (EDXS) by means of a Super X-EDXS detector (FEI Company), elemental mappings of different elements were obtained, in order to gain information about the elemental distribution with high spatial resolution. Line scans and elemental mappings were obtained by evaluating the peak intensity, that is, the area under either the Kα- (O, F, Na, Al, Si) or Lα- (La, Tm) edges of the respective elements, with an automatic routine provided by the commercially available software Esprit1.8 (Bruker Company). More experimental details can be found in [11].

XANES and EXAFS spectroscopies were performed in the beam line BM25 (Spanish-SpLine CRG) at the European Synchrotron Radiation Facility (ESRF) in Grenoble. Measurements were carried out in transmission mode at room temperature. Powder samples of particles sizes ≤60 μm of the glass and the two glass-ceramics were prepared. XAS spectra were collected at the Tm–L_3 edge (8648 eV), recording the absorption in the XANES and EXAFS range, from 8500 eV to 9200 eV. Additionally, XAS spectra of powder samples of pure Tm_2O_3 and TmF_3 as reference compounds were also recorded in the same conditions. All the spectra were analysed and fitted using the Athena and Artemis softwares that allows the accurate selection of the analysis ranges and parameters. More experimental details can be found in [12].

Results and Discussion

(Scanning) Transmission electron Microscopy ((S)TEM) and energy dispersive X-ray spectroscopy (EDXS) of the parent glass and the glass-ceramic

Fig. 3a shows a STEM micrograph and the corresponding EDXS elemental distribution maps of the parent glass. It is clearly observed phase-separated La-enriched region as droplets with diameters of around 30 - 40 nm, as previously reported in [8]. The mappings indicate that Si and Al are distributed over the whole glassy matrix, although a light depletion of these elements is observed in the centre of the droplets. The phase-separation droplets certainly contain La and F, as expected from previous works [2, 8]. La is highly concentrated in the phase-separation droplets, although a small quantity remains in the rest of the glassy matrix. Fluorine is found both in the phase separation droplets as well as in the matrix. This F distribution agrees with the ^{19}F NMR data from this glass reported in ref. [5], in which it is stated that fluorine is distributed between La-F and Al-F-Na bonds. Finally, the Tm map in Fig. 3 clearly shows that Tm is incorporated and enriched in the amorphous phase-separation droplets, although there is still a significant Tm-content in the matrix.

At this point, it is worth mentioning that the possibility of actually being able to map the distribution of as little as less than 1 mol % of Tm (with respect to the other elements that the sample consists of) in a radiation sensitive sample is a very difficult task and has been successfully carried out. It is only possible through a combination of proper sample preparation, cutting-edge analytical transmission electron microscopy at reduced acceleration voltage and, particularly, the application of an EDXS detector system such as that used for these experiments. From the optical point of view, this F-enriched environment around Tm (i.e., the phase-separation droplets) already in the glass, explains an up-conversion emission that is only slightly less intense to that of the glass-ceramic reported in [8].

During the annealing of the parent glass at 620 °C for 40 h, LaF_3 nano-crystals precipitated in a residual glassy matrix (Fig. 3b, Fig. 4), with a homogenous size distribution (crystal diameters of ca. 10-20 nm). The crystallites are smaller than the preceding droplets. Indeed, up to four crystallites were observed within the volume of a precursor drop [8], the crystal size distribution being quite narrow.

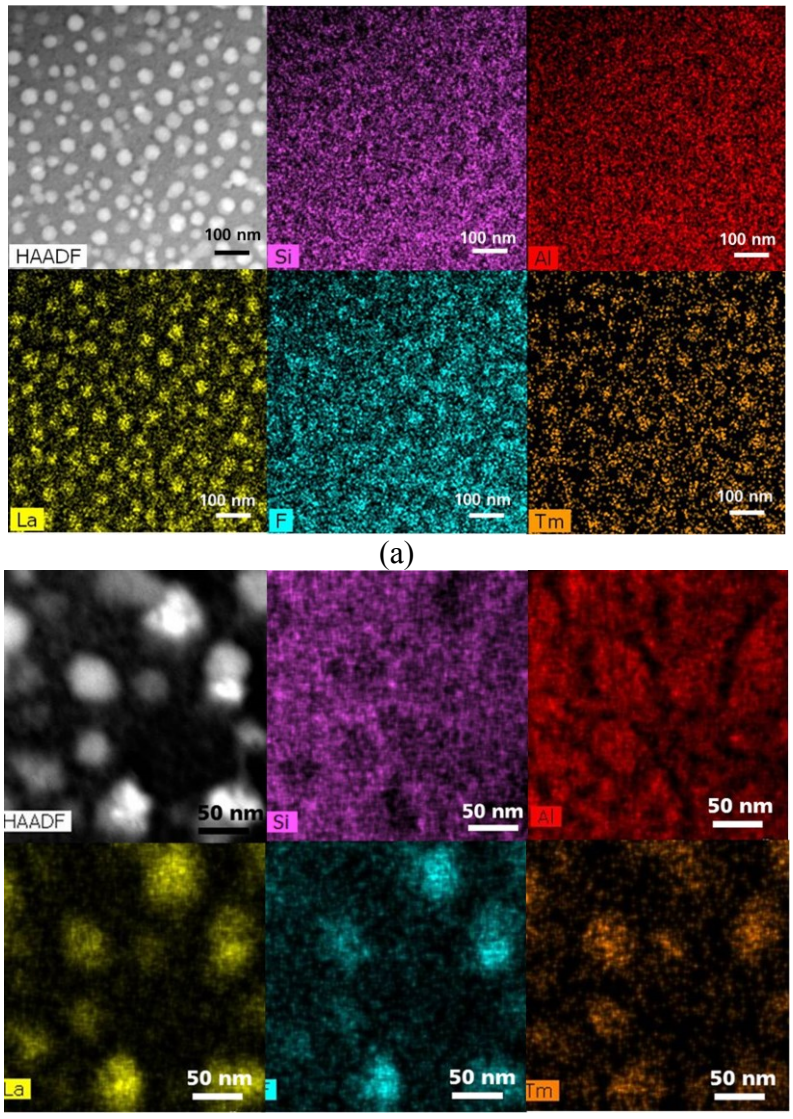

Figure 3: EDXS elemental distribution mapping of the Tm^{3+} doped (a) glass and (b) glass-ceramic obtained at 620 °C during 40 h [11].

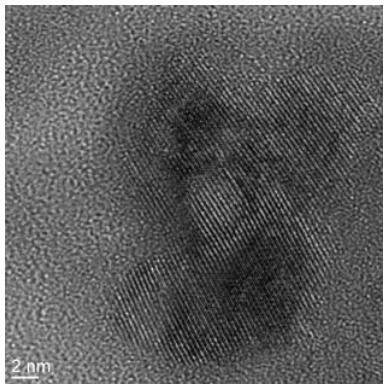

Figure 4: High Resolution micrograph of a LaF_3 nano-crystal in a glass-ceramic obtained at 620°C for 40 h [11].

The crystallisation mechanism suggests that the liquid-liquid phase-separation droplets in the glass develop into LaF_3 nano-crystals upon annealing [8]. EDXS elemental mappings were also acquired for the glass-ceramics (Fig.3b). Si clearly occupies the residual glassy matrix. Si is depleted in the center of the crystalline areas, while the edges of the crystal agglomerates are enriched in this element. Al is distributed across the entire area analyzed, but some enrichment of this element can be observed at the periphery of the crystals, forming a first shell. The mappings prove that the crystals contain La and F. Tm is enriched in the LaF_3 crystals, but some thulium remains in the glassy matrix, which, as previously mentioned, is very relevant from the optical point of view, and is in good agreement with our previous results [8].

From these results and those of ref.[8] the crystallisation mechanism can be described more precisely as follows (Fig.5): The parent glass contains La- and F-enriched phase separation droplets, also containing Si-, Al- and O. The doping ion Tm^{3+} is partially incorporated in the phase-separation regions. Al is present, likely as Al_2O_3, in a thin shell surrounding the droplets. Upon annealing, the growth of the LaF_3:Tm crystallites within these phase separation droplets takes place.

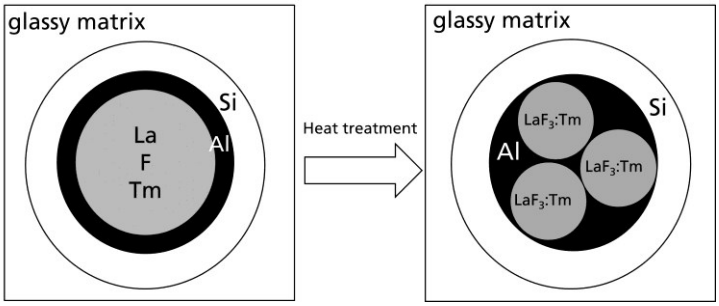

Figure 5 : Scheme of the nano-crystallisation mechanism in the studied Tm^{3+} doped glass.

Quantification of the Tm^{3+} incorporation in LaF_3 nano-crystals by X-Ray Absorption Spectroscopy (XAS): XANES and EXAFS

Fig. 6 displays the normalised XANES spectra at the Tm–L_3 edge for the Tm-doped glass and glass-ceramics treated during 10 and 40 h. A detailed analysis of the spectra revealed slight differences in the edge position, and in the width and intensity of the white line (first maximum above the edge). The absorption edge was fitted to a Lorentzian function yielding the parameters that are summarised in Table 1.

The position of the absorption edge (defined as the maximum of the derivative spectra) for the initial glass is 8649.6 eV, that corresponds to $Tm^{3+,}$ discarding the presence of significant amounts of Tm^{2+} in this glass. Upon annealing, this edge shifts toward higher values, being 8650.9 eV and 8651.7 eV, for the samples annealed 10 h and 40 h, respectively. This shift to higher values in the glass-ceramics respecting to glass, increasing with treatment time (Table 1) provides a further evidence of a fluorine enriched environment of Tm^{3+} ions in the glass-ceramics upon annealing. XANES spectra measured at the Tm–L_3 edge of the reference samples Tm_2O_3 and TmF_3 were also recorded [12]. The edges are located at 8649.7 eV and 8651.2 eV for Tm_2O_3 and TmF_3, respectively. Indeed, E_0 in the glass coincides with E_0 of Tm_2O_3 (8649.7 eV), shifting to that of TmF_3 (8651.2 eV) in the glass-ceramics. This also indicates the diffusion of Tm^{3+} ions from the glass matrix to the LaF_3 crystals during the crystallisation process. Additionally, the decrease of the width of Tm^{3+} absorption edge peak, FWHM, from the glass to the glass-ceramics (Table 1), is also a fingerprint of a higher environmental symmetry.

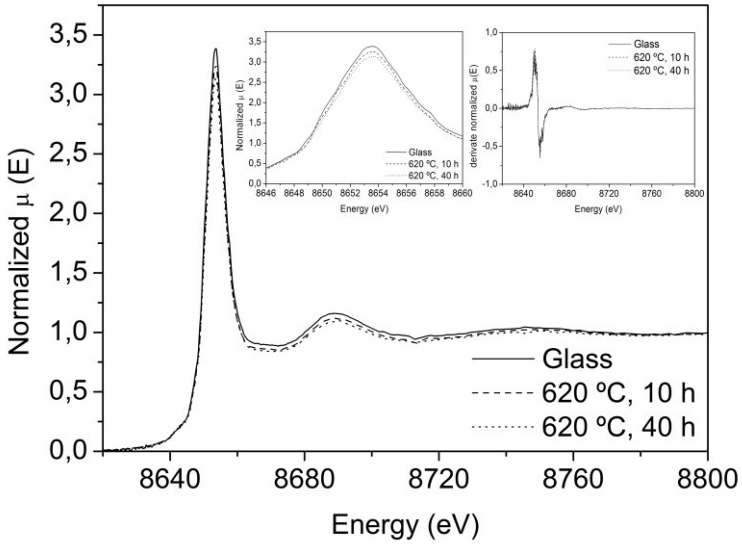

Figure 6: Normalised Tm–L_3 edge XANES spectra of glass and glass-ceramics obtained at 620 °C for 10 and 40 h. A better resolution of the absorption edge and the derivate function of μ(E) are shown in the onset [12].

Table 1: Absorption energy E_0, derived from the derivate function of μ(E) in Fig.6, and FWHM of the Lorentzian function used to fit the Tm- L_3 absorption edge [12].

	Glass	**620°C-10 h**	**620°C-40 h**
E_0 [eV]	8649.6	8650,9	8651.7
FWHM	5.29	5.18	5.00

In order to quantify the modification of Tm local environment during crystallisation, the XANES spectra of the annealed samples were fitted by using the Athena software to a linear combination of the spectrum of the reference parent glass, where most of Tm^{3+} ions are incorporated in the oxygen rich glassy phase, and that of the TmF_3 reference sample in which the Tm ions are in a fluorine environment. In this way, we may quantify the fraction of Tm^{3+} entirely surrounded by fluorine atoms, that is, Tm ions incorporated in the LaF_3 nanocrystals by diffusion during the crystallisation process. Fig. 7 shows the results of these fits. For the sample treated during 10 h (not shown), 17 mol. % of the Tm cations are incorporated in the nanocrystals. When the annealing time is prolonged up to 40 h, (Fig.7) the fraction of Tm in the LaF_3 nanocrystals increases up to 30 mol. %. This confirms the tendency of Tm to preferentially incorporate into LaF_3 nanocrystals substituting La^{3+} due to the similar size and identical charge, and explains the enhanced optical properties of these materials reported in Ref.[8].

Taking into account the volume fraction of LaF_3 nanocrystals in the glass-ceramics, it is possible to calculate the concentration of Tm^{3+} in both the nanocrystals and glass matrix. Thus, $[Tm^{3+}]_{nc}/[Tm^{3+}]_g$ goes from 6 on the glass-ceramic treated 10 h to 12 on the material treated during 40 h, showing the high concentration of thulium ions in the crystalline fluoride environment.

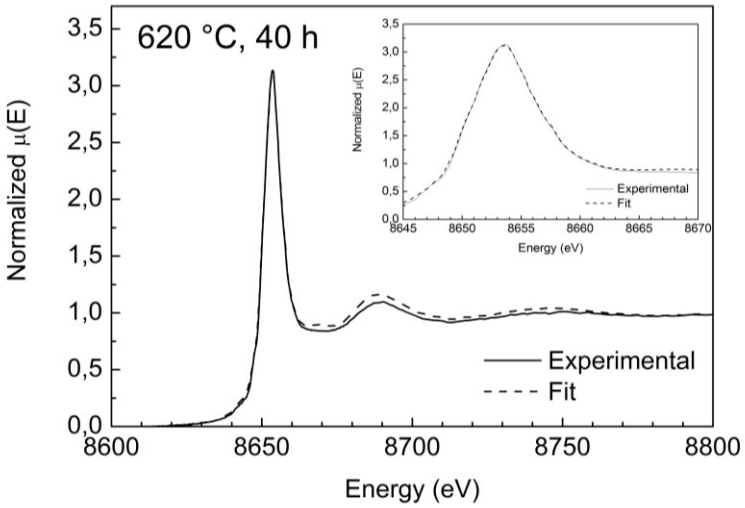

Figure 7: Fit of the experimental XANES spectra of the glass-ceramic obtained at 620 °C during 40 h to a linear combination of the spectra of the initial glass and TmF_3 reference. To a better show the quality of the fit, an insert in the range 8600–8800 eV has been added [12].

The analysis of the EXAFS spectra was performed with Artemis for the TmF_3 reference sample as well as for the glass and the glass-ceramic obtained at 620 °C for 40 h. The results for the fitting in the k and real spaces are displayed in Fig. 8. The fitting parameters are: the interatomic distance, the coordination number N, the Debye–Waller factor value σ2 and the absorption energy E_0, that are summarised in Table 2. Only the first neighbours have been fitted in each spectrum in a single scattering approximation. The spectra have been modelled by considering a single shell model of equidistant F ions in case of TmF_3 and equidistant O ions in the glass spectrum. For the glass-ceramic spectrum, a first coordination shell as combination of O and F atoms was modelled, by combining the spectra of the TmF_3 reference sample (Tm–F environments) and that of the glass (Tm–O environments). The distances Tm–F in the TmF_3 reference sample and Tm–O in the glass are quite similar and differ only in a few hundredths, within the error margin. The distance Tm–O in the glass-ceramic slightly increases with respect to that in the glass, while the Tm–F distance in the glass-ceramic is practically the same value of Tm–F in the reference TmF_3, supporting a partial location of Tm in a fluoride environment.

That is, the current approach considered for the glass-ceramic 620°C–40 h was a O_m–Tm–F_n structure, trying to get the mean number of F and O neighbours corresponding to a first coordination shell. This approach does not consider the crystalline or glassy structure in which Tm ions are included. In this model, the mean first neighbours of the Tm ions have been determined to be a 27% in F, which agrees with the 30% obtained from XANES analysis in the error margin. In this case, the F ions have been assumed to occupy a first shell placed at 2.28 Å and the O ions at 2.8 Å. In this work, a Tm–F distance of 2.28 Å agrees with an incorporation of Tm^{3+} in the LaF_3 lattice, shortening the bond distance due to its smaller radius compared with that of La^{3+}. When normalising the coordination number N of Tm in the environments Tm–O and Tm–F in this glass-ceramic with the scattering amplitude factor of the Tm–F bonds, it is possible to get a semi-quantitative evaluation of the Tm ions incorporated in the LaF_3 structure. In this case, considering the relative coordination number of O respect to F in the Tm, it is possible to estimate this as 27 mol. % of Tm ions in this environment. Taking into account the estimated error of 20% in N, this estimation fully agrees with the 30 mol. % obtained from the XANES fittings. A partial diffusion of Tm^{3+} ions from the glass matrix to the LaF_3 nanocrystals, supported by diverse evidences from EXAFS and XANES data, can be concluded.

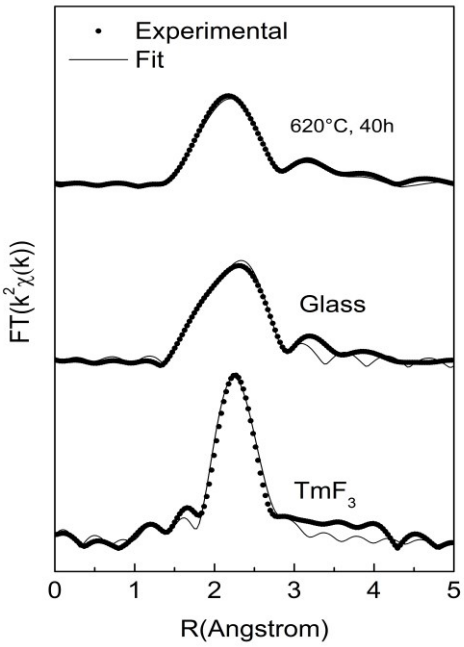

Figure 8: Fits in the k2-χ(k) function (A) and the FT(k2-χ(k)) function (B) of the TmF_3 reference sample, glass and glass-ceramic obtained at 620 °C during 40 h [12].

Table 2: The nearest neighbour's structural parameters obtained by the curve fitting the experimental EXAFS Spectra in Fig.8 [12].

Sample	Shell	R (A)	N	σ^2 (10^{-3} Å)	ΔE_0 (eV)
TmF_3	**Tm-F**	2.25	7.1	5.9	-1.88
Glass	**Tm-O**	2.28	8.1	1.8	2.83
620 °C- 40h	**Tm-O**	2.81	5.8	3.4	7.0
	Tm-F	2.24	2.4	3.4	3.9

Summary

The identification of Tm^{3+} ions environment in a Tm^{3+} doped-oxyfluoride glass and two derived glass-ceramics has been carried out by using HR-TEM and EDX techniques, together with XAS measurements.

The parent glass is constituted by ca. 30 nm amorphous phase separation regions containing La and F. The dopant ion Tm^{3+} is partially included in both, the glass matrix and the phase separation droplets. The near surrounding of the droplets is enriched in Al and Si. After the heat treatment of the parent glass, LaF_3 nano-crystals are developed in the droplets, originally enriched in La, F and Tm. Fluoride crystals act as main host for the Tm^{3+} ions.

Thanks to the advanced STEM/ EDSX analysis, it was possible to identify a thin Al enriched layer around the crystals and a second shell enriched in Si, both inhibiting further crystal growth, enabling to maintain the nanocrystal size.

The detection of Tm^{3+} ions in the LaF_3 nano-crystals through EDX elemental mappings is a great advance in the understanding of RE doped glass-ceramics, since it is the key feature of these materials for their application in optical devices. XANES and EXAFS experiments confirmed that upon thermal treatments, the Tm^{3+} incorporates preferentially into the LaF_3 nanocrystals. This incorporation increases with the treatment time. In particular, for 10 h treatment the incorporation of Tm ions in the LaF_3 nano-crystals is about ~17%, while increasing the thermal treatment time to 40 h near 30% of the Tm cations is incorporated in the nano-crystals.

Acknowledgements

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